

PATENT ABSTRACTS OF JAPAN

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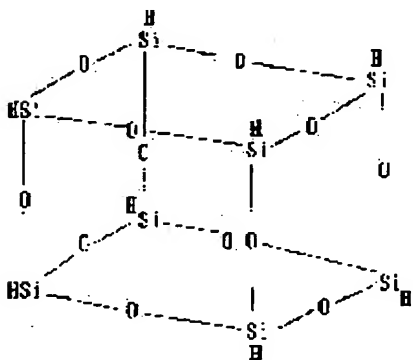
(72)Inventor : ZANK GREGG ALAN
SUDO MICHITAKA(54) PRODUCTION OF ORGANIC-SOLVENT-SOLUBLE HYDROGENATED
OCTASILSESQUIOXANE/VINYL GROUP-CONTAINING COPOLYMER

(57)Abstract:

PROBLEM TO BE SOLVED: To produce an organic-solvent-soluble copolymer which is excellent in insulation properties, resistances to heat and oxidation, weatherability, etc., and is useful for impregnation materials, interlayer materials, and coating or molding materials by reacting a hydrogenated octasilsesquioxane with a divinyl compound in a specified ratio in the presence of a hydrosilylation catalyst.

SOLUTION: One mol of a hydrogenated octasilsesquioxane represented by the formula is reacted with a divinyl compound represented by $\text{CH}_2=\text{CH}-\text{L}-\text{CH}=\text{CH}_2$ [wherein L is a 3-10C divalent hydrocarbon group or $-(\text{SiR}_2\text{O})_m-\text{SiR}_2-$ (wherein m is 1-10; and R is a 1-6C alkyl or 6-9C aryl)] in an amount of 0.2 mol or higher but lower than 3 mol in the presence of a hydrosilylation catalyst preferably in a molar ratio to the

vinyl groups of the divinyl compound of 1/100,000-1/100. Examples of the catalyst are platinum chloride, chloroplatinic acid, a platinum-olefin complex, a platinum-phosphine complex, a platinum-vinylsiloxane complex, and the solutions of these compounds.



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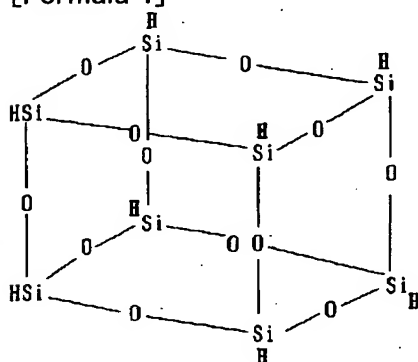
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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the hydrogenation OKUTA silsesquioxane-vinyl group content compound copolymer of the organic solvent fusibility characterized by making the vinyl group content compound (B) expressed with the following general formula (2) react in 0.2 mols or more and less than three mols to one mol of the hydrogenation OKUTA silsesquioxane (A) expressed with the following general formula (1) under existence of a high DOROSHI relation catalyst.

[Formula 1]



…式 (1)

$\text{CH}_2=\text{CH}-\text{L}-\text{CH}=\text{CH}_2$ -- Formula (2)

here -- L -- a degree (a) -- or (b) -- from -- it is chosen.

(a) Divalent (hydrocarbon-group b)-(SiR₂O)_m-SiR₂-m:1 ≤ m ≤ 10 R of carbon numbers 3-10 is the alkyl group of carbon numbers 1-6, or the aryl group of carbon numbers 6-9 independently, respectively.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the organopolysiloxane of the organic solvent fusibility which has basket type structure, especially the manufacture approach of an OKUTA silsesquioxane content copolymer.

[0002]

[Description of the Prior Art] Conventionally, since it excels in thermal resistance, electric insulation, flame resistance, weatherability, etc., organopolysiloxane is used as the resist ingredient of a semi-conductor, the insulating material for motors, the sinking-in insulating material for transformers, a coating, a primer, etc. (refer to Nikkan Kogyo Shimbun edited "a silicone handbook" by Kunio Ito, and 1990 issue). The thing of various presentations and structure is known and, as for organopolysiloxane, the physical properties are also rich in change.

[0003] However, these electrical and electric equipment and electronic ingredients are asked for the improvement of the further property. Insulation, thermal resistance, endurance, etc. are raised as such a property.

[0004] The following advanced technology is known about the manufacture approach of the copolymer which uses silsesquioxane as a copolymerization component. Lichtenhan etc. polyhedron oligo MERIKKU silsesquioxane (polyhedral oligomeric Silsesquioxane) it is indicating about the manufacture approach of the copolymer which constructed the bridge with the silane of two functionality which makes an amine etc. a functional group, the siloxane, or the organometallic compound (association) (U.S. Pat. No. 5,412,053 specifications, such as Lichtenhan.J.D.; Gilman and J.W., --) "Chem.Mater.", such as U.S. Pat. No. 5,589,562 specifications, such as Lichtenham.J.D. and Gilman.J.W., and Lichtenhan.J.D., -- 1996, 8, and 1250-1259.

[0005] Each of them is what has a deficit in the basket type structure (cage) of silsesquioxane, and the so-called imperfect basket type structure (not the shape of perfect 8 face pieces but structure in which the one section suffered a loss). It indicates about the manufacture approach of the copolymer which combined the thing by the siloxane.

[0006] Moreover, the manufacture approach of the copolymer which Lichtenhan.J.D. etc. used as the pendant copolymerization component the manufacture approach of the copolymer which uses as a principal chain what combined the silsesquioxane of imperfect basket type structure by the siloxane etc., and the silsesquioxane of basket type structure, and used the methacrylic acid as the copolymer principal chain component is indicated ("Comments I norg.Chem." 1995 17,115-130).

[0007] Furthermore, Lichtenhan.J.D. etc. is indicating the manufacture approach of OH combined with Si located in the corner of the imperfect basket type structure of silsesquioxane, and the silsesquioxane-siloxane copolymer to which the screw (dimethylamino) silane etc. was made to react ("Macromolecules", 1993, 26, 2141-2142).

[0008] The manufacture approach of the copolymer to which the silsesquioxane of perfect basket type structure and other compounds are made to react on the other hand is indicated as advanced technology ("Macromolecules(es)", such as U.S. Pat. No. 5,484,867 specifications, such as Lichtenhan.J.D., J, and W., and Alan Sellinger, 1996, 29, p2327 -2330 reference). [0009] On U.S. Pat. No. 5,484,867 specifications One vinyl group content compound is combined with the corner of the silsesquioxane of perfect basket type structure. Furthermore, the compound (refer to the 6th column type (2)) Carry out graft polymerization to other copolymers through said vinyl group. The manufacture approach (refer to this 13th column and the 14th column) of a graft copolymer of having the pendant of silsesquioxane, Copolymer which has a vinyl group to both ends in a list (B) And said vinyl group content silsesquioxane compound (A) Silsesquioxane addition ABA mold block copolymer obtained by the reaction of vinyl groups (refer to this 8th column) The manufacture approach is indicated. Moreover, there is a general publication that variants, such as a substituent, affect the heat characteristic of the copolymer obtained, solubility, etc.

[0010] It is indicated by above-mentioned " "Macromolecules", 1996 and 29, and p2927-2330" by carrying out high DOROSHI relation (hydrosilylation) of propargyl methacrylate and the silsesquioxane of basket type structure that what the manufacturing method of the basket type silsesquioxane which introduced the methacrylate radical into two or more **** was indicated, and was obtained by the approach is meltable to an organic solvent.

[0011] However, the method of manufacturing the copolymer of fusibility which each above-mentioned reference was made to react and combine the hydrogen of hydrogenation OKUTA silsesquioxane and one [which has a vinyl group to both ends / at least] vinyl group of a compound by hydrosilylation, and connected one or more hydrogenation OKUTA silsesquioxane is not indicated.

[0012] Moreover, it has reported that the copolymer which Hoebbel etc. indicated the manufacture approach of the perfect basket type silsesquioxane compound which combined the vinyl group with two or more corners of a basket through Si-O-association, and was obtained from the compound serves as transparent gel (namely, the obtained copolymer is not fusibility). (D. J.Non-Crystalline Solids 176 (1994), such as Hoebbel, 179-188) .

[0013] Furthermore, I.Hasegawa is indicating about the approach of manufacturing the compound only combined by the dimethylsilyl radical without breaking the basket type structure of silsesquioxane (I. Hasegawa;J.of Sol-Gel Sci.and Technol.(1995) 5 (2), 93-100).

[0014] About the manufacturing method of the copolymer to which the hydrogenation silsesquioxane (namely, hydrogenation OKUTA silsesquioxane) which has basket type structure, and the compound which has a vinyl group to the both ends pinpointed by the formula (2) are made to react by the hydrosilylation reaction and which has hydrogenation OKUTA silsesquioxane in the principal chain of organic solvent fusibility, it is indicated by neither of well-known reference as above. Moreover, a copolymer which is equipped with the thermal resistance which was excellent beyond said well-known technique, weatherability, oxidation resistance, etc., and has the outstanding insulation was desired.

[0015]

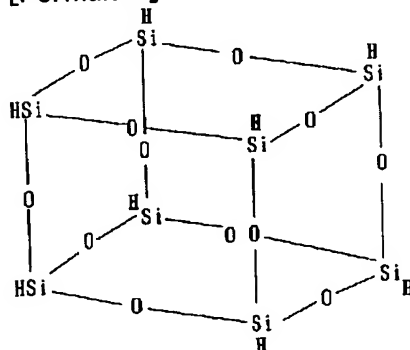
[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the

approach of manufacturing the copolymer ("the copolymer obtained by the manufacture approach of this invention" being called hereafter) of organic solvent fusibility to which the ingredient corresponding to said request, i.e., hydrogenation OKUTA silsesquioxane, and the compound which has a vinyl group to both ends were made reacting by hydrosilylation. Here, it can be said that the compound which has a vinyl group to both ends is a monomer component which constitutes a copolymer, and is a cross linking agent in the semantics which has the operation which combines two or more hydrogenation OKUTA silsesquioxane.

[0016]

[Means for Solving the Problem] This invention is a high DOROSHI relation catalyst (hydrosilylation catalyst). As opposed to one mol of the hydrogenation OKUTA silsesquioxane (A) expressed with the following general formula (1) under existence The vinyl group content compound expressed with the following general formula (2) (B) (in this application, "a divinyl compound (B)" is called hereafter.) It is the manufacture approach of the hydrogenation OKUTA silsesquioxane-vinyl group content compound copolymer of the organic solvent fusibility manufactured by making it react in 0.2 mols or more and less than three mols.

[Formula 2]



…式 (1)

$\text{CH}_2=\text{CH}-\text{L}-\text{CH}=\text{CH}_2$ -- Formula (2)

here -- L -- a degree (a) -- or (b) -- from -- it is chosen.

(a) The divalent hydrocarbon group of carbon numbers 3-10 and (b)-(SiR₂O)_m-SiR₂-m:1 <=m<=10R are the alkyl group of carbon numbers 1-6, or the aryl group of carbon numbers 6-9 independently, respectively.

[0017] Hydrogenation OKUTA silsesquioxane (A) has basket type structure, and the hydrogen atom has combined it with Si atom which constitutes the corner of a basket so that it may be expressed with a formula (1). This invention offers the approach that the description on the structure of both components can be harnessed, by using said divinyl compound (B) as a part for the bond part of said hydrogenation OKUTA silsesquioxane (A) (mutual mold block-copolymer component).

[0018] A hydrogenation OKUTA silsesquioxane-vinyl group content compound copolymer has a property (for example, reinforcement and an electrical property) originating in hydrogenation OKUTA silsesquioxane (A), and the flexibility originating in a divinyl compound (B) by the manufacture approach of this invention. For this reason, this copolymer can be applied to the application of a sinking-in ingredient, the ingredient between layers, a coat, or a molding material, and the outstanding insulating property, thermal resistance, reinforcement, etc. can be demonstrated.

[0019] After the hydrogenation OKUTA silsesquioxane-vinyl group content compound copolymer obtained by the manufacture approach of this invention is applied to a necessary

part in modes, such as spreading, restoration, or shaping, it is considered that SiH of a basket type structure corner forms siloxane association between SiH(s) of other basket type structure corners by natural neglect or moderate heating. Consequently, the copolymer obtained by this invention can serve as the coat with which three-dimensions network structure was built, and it excelled in the mechanical characteristic, and stability, thermal resistance, oxidation resistance, and an insulating property have been improved, a layer, a Plastic solid, and a layer insulation ingredient.

[0020] When a hydrogenation OKUTA silsesquioxane compound (A) reacts to the divinyl compound (B) of the ratio specified by the manufacture approach of this invention, a hydrogenation OKUTA silsesquioxane-vinyl group content compound copolymer is obtained. Here, by using this specific divinyl compound (B), softness and flexibility are introduced into said copolymer and each above-mentioned property is improved in multiplication. In the case of for example, an insulating paint film, the flexibility introduced into this copolymer offers the ease of carrying out of paint, forms a paint film without a defect, and produces the toughness of the coat obtained further.

[0021] Generally, crystallinity was high, hydrogenation OKUTA silsesquioxane also had it, and, for this reason, OKUTA silsesquioxane was not easy to obtain a good coat by the hydrogenation OKUTA silsesquioxane independent. [same] The hydrogenation OKUTA silsesquioxane-vinyl group content compound copolymer obtained by the manufacture approach of this invention is amorphous nature, and became possible [demonstrating the outstanding properties (a mechanical characteristic, an electrical property, hardenability, etc.) which hydrogenation OKUTA silsesquioxane has in an organic solvent further since it is fusibility in the application of many including an insulating material].

[0022] After the copolymer obtained by the manufacture approach of this invention is applied to a base material, SiH which the OKUTA silsesquioxane structure of this copolymer has hardens it by forming Survival SiH and siloxane association which other OKUTA silsesquioxane has. This hardening reaction generates hydrogen gas as a by-product depending on an ambient atmosphere or conditions. For example, after actually being applied on an electronic substrate or a silicon wafer in the case of an insulating material, in severe conditions, such as an elevated temperature, a by-product may arise by the reaction of unreacted functional groups. Even if a by-product arises in the case of the copolymer obtained by the manufacture approach of this invention, it is a point advantageous to whether it is ** that it is hydrogen gas in respect of maintenance of the effect which it has on the candidate for application, the electrical property of the insulating material itself, or a mechanical characteristic compared with the insulating material in which the matter containing a carbon atom or a chlorine atom carries out a byproduction.

[0023] a formula -- L in the divinyl compound (B) specified by (2 [CH₂=CH-L-CH₂=CH]) -- degree (a) Or (b) from -- it is chosen.

(a) Divalent (hydrocarbon-group b)-(SiR₂ O) m-SiR₂-m:1 <=m<=10R of carbon numbers 3-10 is the alkyl group of carbon numbers 1-6, or the aryl group of carbon numbers 6-9 independently, respectively.

[0024] An improvement of physical properties is not enough by the reasons of the flexibility of the copolymer obtained becoming scarce, when a monomer component tends to volatilize and the complexity on handling can also be hung down, if there are few carbon numbers of the hydrocarbon group of the above (a) than 3. Moreover, if a carbon number exceeds 10 on the other hand, the rate of the hydrogenation OKUTA silsesquioxane of the basket type structure in

a copolymer will decrease relatively, and it is fully hard to demonstrate the various properties which the copolymer of said this invention has. As long as the copolymer which the hydrocarbon group of the above (a) reacts with SiH of the basket type structure corner of hydrogenation OKUTA silsesquioxane, and is obtained by the approach of this invention can demonstrate expected effectiveness, you may be any of the aliphatic hydrocarbon radical of the shape of the shape of a straight chain, and branching, and an aromatic hydrocarbon radical, and a part of substituents may be a carbon atom and different atoms other than a hydrogen atom, for example, F, Si, O, etc. When choosing an aromatic hydrocarbon radical as a hydrocarbon group, it is desirable at the point whose thermal resistance improves. In addition, when a reaction with SiH of the corner of basket type structure is taken into consideration, as for the above-mentioned aliphatic hydrocarbon radical, it is desirable that it is a saturated-aliphatic-hydrocarbon radical.

[0025] It is also the same reasons to be one or more and to have made m or less into ten about the repeat unit of the siloxane of the above (b), and to have specified R. When an aryl group is chosen about R, it excels in thermal resistance [else].

[0026] if a more detailed general formula shows L under above (b) $-R_3 R_4 Si-O-SiR_3 R_4-$ and $-(R_3 R_4 SiO)_n-SiR_3 R_4-$ [— R₃ and R₄ are the straight chain of carbon numbers 1-6, the alkyl group of branching or the aryl group of carbon numbers 6-9, and n = 2 - 10] independently among a formula, respectively.

[0027] The example of a divinyl compound (B) expressed with a general formula (2) is shown below. When it is that as which L is chosen from the above (a) in a general formula (2), specifically $CH_2=CH-(CH_2)_3-CH=CH_2$ and $CH_2=CH-(CH_2)_4-CH=CH_2$, $CH_2=CH-(CH_2)_5-CH=CH_2$ and $CH_2=CH-(CH_2)_6-CH=CH_2$, $CH_2=CH-(CH_2)_7-CH=CH_2$ and $CH_2=CH-(CH_2)_8-CH=CH_2$, $CH_2=CH-(CH_2)_9-CH=CH_2$ and $CH_2=CH-(CH_2)_{10}-CH=CH_2$, $CH_2=CH-Ar-CH=CH_2$ (1, 4-divinylbenzene), $CH_2=CH-Ar F_4-CH=CH_2$ (1, 4-divinyl - 2, 3, 5, 6, tetrafluoro benzene), $CH_2=CH-CH_2-C(CH_3)_2-CH_2-CH=CH_2$ etc. — it can illustrate (Ar shows a phenylene group among said formula, and Ar F₄ shows a tetrafluoro phenylene group). When L is what is chosen from the above (b), similarly moreover, specifically $CH_2=CH-Si(CH_3)_2OSi(CH_3)_2-CH=CH_2$, $CH_2=CH-(CH_2)_4-CH=CH_2$ and $CH_2=CH-[Si(CH_3)_2O]_xSi(CH_3)_2-CH=CH_2$, $CH_2=CH-Si(Ph)_2OSi(Ph)_2-CH=CH_2$ etc. — it can illustrate (inside of said formula; it is x =2-10 and Ph shows a phenyl group).

[0028] It is required to make a divinyl compound (B) react in 0.2 mols or more and less than three mols to one mol of hydrogenation OKUTA silsesquioxane (A). If a divinyl compound (B) is made into three mols or more, the copolymer obtained will serve as gel and the solubility to an organic solvent will be lost. The divinyl compound (B) of the twist many which a divinyl compound (B) needs for the corner of the hydrogenation OKUTA silsesquioxane of basket type structure when superfluous adds it, and it is considered to be the cause that the structure of cross linkage of the twist many to need is formed. Mechanical properties, such as thermal resistance, electric insulation, flame resistance, weatherability and reinforcement, and toughness, worsen, and it becomes impossible for the product to have many of these properties required as an insulating ingredient, without being formed in extent which the structure of cross linkage needs on the other hand as it is less than 0.2 mols.

[0029]

[Embodiment of the Invention] In order to make this invention much more easy to understand, the examples and the examples of a comparison of this invention including the example of manufacture of the hydrogenation OKUTA silsesquioxane used as the raw material in the

manufacture approach of this invention are shown. However, it cannot be overemphasized that it is not what should limit this invention only to those operation gestalten by these.

[Process of hydrogenation OKUTA silsesquioxane] According to the approach of JP,43-31838,B and example 1 publication, in the process which manufactures a solid-state resin-like polymer, the insoluble matter which filtered the benzene solution and was obtained was extracted after washing until it became neutrality about the benzene phase, and it washed by the hexane. And the insoluble matter was analyzed by the following approach to this hexane.

[0030] GPC was carried out by the Toso chromatograph which possesses a TSKgel G2000HHR column and toluene as a mobile phase. 1 The NMR spectrum of ¹H and ²⁹Si was recorded on the Bruker300MHz spectrometer. By the graphite monochromator and the CuK alpha emission, it is Jeol. It analyzed by X-ray diffraction with JDX-3530 diffractometer. GC mass analysis was performed by the Shimazu GC-MSQP1000EX chromatograph using DB-5 column. When a temperature up was carried out to 300 degrees C and it held for 30 minutes by part for initial temperature [of 80 degrees C], and 40 degrees-C/of temperature rises, it dissociated best.

[0031] The result of the analysis is as follows.

[Identification data]

MS: (M-H) <-;m/z=423d.IR(Nujolmull, KBrplates):2290(s)1140(vs)918(w)885(sh)870(s)29SiNMR(C6 D6, 4 (CH3) Si=0, Cr(acac)30.026M):delta=-84.452 (s).

MS: Mass spectrum IR: Infrared absorption spectrum

[0032] According to the data of the above-mentioned analysis result, it was checked that the matter insoluble to a hexane obtained by said process is hydrogenation OKUTA silsesquioxane (H T8).

[0033] The reaction of [composition of hydrogenation OKUTA silsesquioxane content copolymer] hydrogenation OKUTA silsesquioxane compound (A) and a specific divinyl compound (B) can be carried out in organic solvents, such as toluene, using the high DOROSHI relation catalyst used for the usual hydrosilylation, addition mold silicone rubber, etc. as a reaction catalyst. A commercial thing can also be used for it although what was manufactured by the above-mentioned approach was used for hydrogenation OKUTA silsesquioxane.

[0034] As an example of the above-mentioned catalyst, a platinum chloride, chloroplatinic acid, a platinum-olefin complex, a platinum-phosphine complex, platinum-vinyl siloxane complexes, and these solutions are mentioned.

[0035] Especially a limit does not have the amount of catalysts used, and although what is necessary is just a complement, an amount which serves as a mole ratio of 1 / 100,000 - 1/100 to one mol of vinyl groups of a formula (2) is suitable for a reaction.

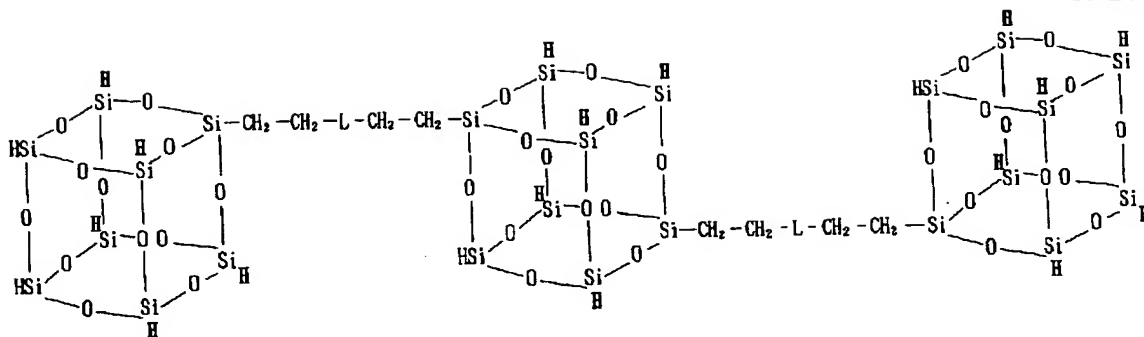
[0036] As an organic solvent, toluene is usually used.

[0037] Reaction temperature is chosen from a room temperature in the range of under the boiling point of an organic solvent. Reaction pressure is performed by ordinary pressure in many cases.

[0038] The repeat unit of the copolymer obtained by the manufacture approach of this invention is shown by the following structure expression.

[0039]

[Formula 3]



Also when the copolymer expressed with the above-mentioned structure expression turns into a copolymer with which the copolymer for which the structure whose beta addition the vinyl group did is shown, and which is obtained by the reaction includes the structure whose alpha addition the vinyl group did although it is, a certain thing is in **.

[0040] the line which reacted by the above-mentioned formula to the hydrogen which a vinyl group has in the location of the diagonal line of hydrogenation OKUTA silsesquioxane — the example of a typical copolymer which shows structure is shown. In the copolymer actually manufactured, when a part of thing which has reacted to three or more hydrogen of hydrogenation OKUTA silsesquioxane coexists, it thinks. Since association of hydrogenation OKUTA silsesquioxane (A) is also easy by using the divinyl compound (B) like the above, said copolymer can be manufactured efficiently. Moreover, compared with the copolymer reaction which forms siloxane association by condensation, there are few amounts of a resultant and the bad influence to final products, such as a coat, is also pressed down. As a result, there are few defects of a coat and the final product of the description which was excellent in electrical properties, such as mechanical strengths, such as toughness, and insulation, at the list is obtained.

[0041] Furthermore, by each reaction components (the die length of a chain, hardness, configuration atom, etc.), a reaction condition, etc., the copolymer obtained by the manufacture approach of this invention becomes insolubility, becomes hard, or becomes flexible. Speaking concretely, generally, being able to obtain the comparatively flexible last copolymer, if the component of a long chain is used as a connected component (bridge formation component). Moreover, in the case of the same connected component of a carbon number, a copolymer with the thing of branching structure harder than a straight chain-like thing is obtained. Moreover, generally, if a bridge formation component increases, a viscous high copolymer will be obtained so much. Although a certain extent can predict the description of the copolymer actually obtained by adjusting these elements, it is not easy to obtain the copolymer of desired description, and sufficient examination is required for it.

[0042] In the manufacture approach of this invention, it is amorphous and it is most important to obtain a soluble copolymer to an organic solvent. It becomes possible like the above to one mol of hydrogenation OKUTA silsesquioxane about the mole ratio of hydrogenation OKUTA silsesquioxane (A) and a divinyl compound (B) by making a specific divinyl compound (B) into 0.2 mols or more and less than three mols.

[0043] To an organic solvent, when it is fusibility, since the copolymer obtained according to this invention manufacturing method can secure viscosity and flexibility with a divinyl compound (B), it can fully demonstrate the insulation and weatherability which are the property of hydrogenation OKUTA silsesquioxane. Consequently, it can use for an application broad as an insulating coat formation ingredient, a weatherproof coated layer ingredient, a binder for layered

insulating coat formation ingredient, a weatherproof coated layer ingredient, a binder for layered products (layer insulation), etc.

[0044] It is also the description of the manufacture approach of this invention that it can adjust by choosing suitably the divinyl compound the viscosity of a copolymer, whose flexibility, etc. are copolymerization components (B), i.e., a joint component, (bridge formation component) according to the application approaches, such as paint, in that case, corresponding to the description of the ingredient made into the purpose.

[0045] Moreover, blending and using other copolymers for the copolymer obtained by the manufacture approach of this invention in the range which does not spoil expected description if needed does not interfere. Moreover, the antioxidant and coloring agent which are usually used in an insulating coat, a weatherproof coat or the binder layer of a layered product, a sinking-in insulating material, etc., a bulking agent, etc. can be added.

[0046] Since the reaction of a reaction component is usually completed and a monomer component is not included, the obtained copolymer has shelf life and can be used as it is. A monomer can also be removed when the reaction is not completed.

[0047] The process in the case of using divinyl tetramethyl disiloxane (ViMe₂ Si)₂ O as a bridge formation component is explained in full detail. The 3 opening reaction flask of 1L of the nitrogen-gas-atmosphere evaporation possessing a magnetic stirring rod and an air-cooling compressor was loaded with hydrogenation OKUTA silsesquioxane 13.5g (0.032 mols) and divinyl tetramethyl [(ViMe₂ Si)₂ Disiloxane O] 5.95g (0.032 mols) dissolved in toluene 700mL distilled from sodium under the Chisso ambient atmosphere. 0.05g (200 ppm of platinum are included at a weight rate) of toluene solutions of the zerovalent platinum complex of divinyl tetramethyl disiloxane was added stirring to this. Keep at 60 degrees C after addition for 20 hours, and it was made to react, and it was cooled after that, was filtered, and was made dryness by the rotation evaporation machine. Furthermore, it dried with ambient temperature under the dynamic vacuum. The hexane of 75mL(s) separated the polymer from hydrogenation OKUTA silsesquioxane with superfluous little *****. Filtration removal of the hydrogenation silsesquioxane (1.7g) which is dissolving slightly was carried out. MIBK is removed from a filtration object by the vacuum. The solid-state copolymer was dried at 40 degrees C by the dynamic vacuum for 3 hours. Yield was 16.26g and was 91.3% of a theoretical value.

[0048] An example is used for below and this invention is explained more to it at a detail. An example is not used for understanding this invention in a detail more, and this invention is not prescribed by these contents.

[0049]

[Example] In the [example 1] 200ml flask, hydrogenation OKUTA silsesquioxane 2.12g (0.005 mols) was dissolved in 100ml toluene. Divinyl tetramethyl disiloxane 0.97g (0.005 mols) was added to this solution, and 0.05g (200 ppm of platinum are included at a weight rate) of toluene solutions of the zerovalent platinum complex of divinyl tetramethyl disiloxane was added further. Stirring under an argon air current after that, it heated to 55 degrees C and the temperature between 20 hours was kept at 55 degrees C. It cooled to the room temperature after reaction termination, and the organic solvent was distilled off under reduced pressure. This polysiloxane was meltable to toluene, chloroform, and methyl isobutyl ketone.

[0050] The property of this polysiloxane is as follows.

29 Si-NMR: d8.44, d(-a and b-ethylene-Me₂ SiO-) d65.60(ethylene-SiO_{3/2}-) d-84.61 (HSiO_{3/2}-)

Fundamentally, hydrogenation OKUTA silsesquioxane is the copolymer combined with the divinyl

compound, and this copolymer has it to an organic solvent. [meltable]

[0051] The divinyl (compound B) [copolymer constituent to [examples 2-9] and [example 1 of comparison] hydrogenation OKUTA silsesquioxane (A); it can also be called a cross linking agent.] Carrying out as the class of ***** and divinyl compound (B) was indicated to Table 1, other conditions carried out examples 2-9 and the example of a comparison like the example 1.

[0052] Hydrogenation OKUTA silsesquioxane 1.50g (0.0035 mols) was dissolved in 100ml toluene in the [example 10] 200ml flask. 0.05g (200 ppm of platinum are included at a weight rate) of toluene solutions of the zerovalent platinum complex of divinylbenzene 0.455g (0.0035 mols) and divinyl tetramethyl disiloxane was added to this solution. It heated to 60 degrees C, stirring under an argon air current after that, and temperature was kept constant for 20 hours. It cooled to the room temperature after reaction termination, and the organic solvent was distilled off under reduced pressure. The polysiloxane was obtained as a white wax-like solid-state. This polysiloxane was meltable to toluene, chloroform, and methyl isobutyl ketone. The property of this polysiloxane is as follows. $^{29}\text{Si-NMR}$: d8.44, d(-a and b-ethylene-Me₂ SiO-) d65.60(ethylene-SiO₃/2-) d-84.61 (HSiO₃/2-)

[0053] It carried out as the compounding ratio of the divinyl compound (B) and the (copolymer constituent) to [example 11] hydrogenation OKUTA silsesquioxane (A) and the class of divinyl compound (B) were indicated to Table 1, and other conditions were made to react like an example 10.

[0054] The 12.7g trichlorosilan (HSiCl₃) solution which dissolved in the toluene of [example 2 of comparison] 150mL was slowly added in the mixture which consists of the toluene of 200mL(s), the 80.3g sulfuric acid (95 - 98% H₂ SO₄), and the 60.4g oleum (15% SO₃) which were stirred violently. Addition of the silane to an acid medium was performed over 6.5 hours. The reaction mixture was poured out into the separating funnel after the completion of addition, and **** was removed. After washing a toluene phase until it became neutrality, the toluene solution was filtered and the 0.1g insoluble matter was obtained. Subsequently, it evaporates, desiccation solidification of the toluene solution is carried out, and it is the 4.9g (97.8% of yield) solid-state-like resin polymer (HSiO 3/2) n. It obtained. This resin was used as "the resin which consists of conventional hydrogenation silsesquioxane" in Table 2.

[0055] 8.5g (it is 0.020 mols by hydrogenation OKUTA silsesquioxane conversion) of a completely meltable solid-state resin-like polymer (hydrogenation silsesquioxane) to the hexane obtained according to the approach of [example 3 of comparison] JP,43-31838,B, and example 1 publication It dissolves in 400ml toluene under an argon ambient atmosphere. 0.05g and 4.0g (0.021 mols) of divinyl tetramethyl disiloxane (Me₂ ViSi) (2 O) are added for the toluene solution (200 ppm of platinum are included at a weight rate) of the zerovalent platinum complex of divinyl tetramethyl disiloxane there. It was made to stir at 60 degrees C for 64 hours. And when this solution was filtered and the residue was decompressed at the room temperature, the gel solid-state was obtained. This thing was insoluble in toluene. Moreover, it was insoluble also to the hexane.

[0056] The description of the copolymer which used hydrogenation silsesquioxane (H T8) and various kinds of divinyl compounds as the raw material acquired by the process of the above-mentioned examples 1-11 and the example 1 of a comparison was summarized in Table 1.

[0057] [Table 1] Description of the copolymer which changed and obtained the mole ratio using hydrogenation OKUTA silsesquioxane (A), (H T8), and various kinds of divinyl compounds (B) [Table 1]

表1 水素化オクタシルセスキオキサン (A) と各種ジビニル化合物 (B) のモル比を変えて得られた共重合体の性状

実施例及び比較例の番号	(上段) ジビニル化合物(B) の種類 (構造) (下段) "T _g " に対するジビニル化合物(B) のモル比 ("T _g " を1モルとして換算)	生成物の性状	数平均分子量	重量平均分子量	T _g [°C]	収率 [%]	450°C での重量損失 [%]
実施例 1	ViMe ₂ SiOSiMe ₂ Vi 1.0	可溶性固体	3090	60100	30	91.3	11
実施例 2	ViMe ₂ SiOSiMe ₂ Vi 0.25	可溶性固体	約1000	約1300			
実施例 3	ViMe ₂ SiOSiMe ₂ Vi 1.5	可溶性固体	3610	93400	70	86.4	
実施例 4	ViMe ₂ SiOSiMe ₂ Vi 2.0	可溶性固体	6360	331400	115	96.2	4
実施例 5	ViPh ₂ SiOSiPh ₂ Vi 0.25	可溶性固体	1020	1360			
実施例 6	ViPh ₂ SiOSiPh ₂ Vi 0.5	可溶性固体	1310	12600			
実施例 7	ViPh ₂ SiOSiPh ₂ Vi 1.0	可溶性固体	2400	108600		93.5	
実施例 8	Vi(Me ₂ SiO) ₂ SiMe ₂ Vi 1.0	可溶性液状	4410	8230	60	84.2	
実施例 9	Vi(Me ₂ SiO) ₂ SiMe ₂ Vi 1.0	可溶性液状	3250	7790	70	92.4	
実施例 10	ViC ₆ H ₄ Vi 1.0	可溶性固体	9670	17540		96.4	
実施例 11	ViC ₆ H ₄ Vi 2.0	可溶性固体	9980	284000			
比較例 1	ViMe ₂ SiOSiMe ₂ Vi 3.0	ゲル状	—	—			

"T_g" : 水素化オクタシルセスキオキサン

Vi : ビニル基

Me : メチル基

Ph : フェニル基

T_g、収率、450°Cの重量損失の各欄において、空欄の箇所は測定を行っていない。

[0058] Although an expected copolymer can be manufactured by making a divinyl compound (B) react in 0.2 mols or more and less than three mols to one mol of hydrogenation OKUTASILSESQUIOXANE (A) by the manufacture approach of this invention, it is the range in which the thing of the range of two mols was suitable for obtaining an organic solvent fusibility copolymer by especially 0.25 mols or more among the range the passage clear from the result shown in Table 1.

[0059] this invention copolymer obtained in the [dielectric constant of various polysiloxane polymers and coat formed by that cause] example 1 and the example 10 and "the resin which consists of conventional silsesquioxane" obtained in the example 2 of a comparison in the list were dissolved in toluene so that it might become with 20 % of the weight of solid content,

respectively, and the spin coat of the toluene solution was carried out to the silicon wafer.

[0060] And the paint film on the wafer was heated at 100 degrees C under nitrogen-gas-atmosphere for 1 hour, and it heated at 200 more degrees C for 2 hours. Next, under the argon ambient atmosphere, it heated with 5-degree-C programming rate for /for 40 minutes. After that, finally the coat was made into 400 degrees C, was heated for 1 hour, and the coat with a thickness of about 500nm was obtained. The result of having changed the frequency about these coats and having measured the dielectric constant is shown in Table 2.

[0061] [Table 2] The coat which consists of various ingredients, and its dielectric constant [Table 2]

表2 各種被膜とその誘電率

被覆材料 誘電率 (周波数)	実施例1で 得られた 本発明 共重合体	実施例10 で得られた 本発明 共重合体	比較例2で得られた 従来の水素化 シルセスキオキサン からなる樹脂
0.1 KHz	2.70	2.77	3.45
1.0 KHz	2.70	2.77	3.45
10.0 KHz	2.70	2.77	3.44
100 KHz	2.68	2.76	3.43
1.0 MHz	2.66	2.75	3.40
10.0 MHz	2.61	2.75	3.37

Equipment used for measurement of a dielectric constant: Hewlett-Packard 4194A Impedance Analyzer

[0062] Especially the dielectric constant in a high frequency has insulation and negative correlation. That is, if a dielectric constant is low, it will become the index which shows that insulation is excellent. The above-mentioned table 2 has a low dielectric constant as compared with other examples of a comparison in a frequency with the especially expensive copolymer obtained by the manufacture approach of this invention, and it is shown that insulation is excellent.

[0063] Moreover, sufficient preservation stability is acquired by keeping the copolymer obtained by the approach of this invention in the condition that moisture cannot be touched. After being applied by means, such as spreading and sinking in, the moisture in air is absorbed, and bridge formation (it warms if needed) progresses, and serves as the layer and coat which hardened and were equipped with the required mechanical and electric (insulation) property. The copolymer obtained by the manufacture approach of this invention has the property which was excellent as an insulating material as above.

[0064]

[Effect of the Invention] This invention can offer the approach of manufacturing the amorphous nature copolymer of organic solvent fusibility from the hydrogenation OKUTA silsesquioxane of basket type structure, and the divinyl compound (copolymer component) which can adjust the description of a copolymer.

[0065] To an organic solvent, the copolymer obtained by the manufacture approach of this invention can fully demonstrate the insulation which is the property of hydrogenation OKUTA silsesquioxane, thermal resistance, and weatherability by viscosity and flexibility being securable with a divinyl compound (B), when it is fusibility. Consequently, mechanical characteristics, such as the stability of the copolymer obtained, oxidation resistance and reinforcement, and

toughness, are also improvable.

[0066] Many of these properties are utilized and it can use for an application broad as an insulating coat formation ingredient, a weatherproof coated layer ingredient, the binder for layered products (layer insulation), a transformer sinking-in insulating material, an insulating molding material, etc. [0067] Although the suitable operation gestalt of this invention was indicated using the specific vocabulary, it is for merely aiming the publication at explanation, and should be understood as the ability of the mode of modification and change to do in the pneuma or the range of a claim.

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